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## (54) ELECTRIC HEATING ELEMENTS

(71) We, SULZER BROTHERS LIMITED, a Company organised under the Laws of Switzerland, of Winterthur, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to electric resistance heating elements made from doped ceramic materials and to their methods of manufacture. Such electric heating elements are used, for example, as ignitor rods in gas turbine combustion chambers, in boiler combustion chambers and as heating elements in industrial and laboratory furnaces and ovens. They are usually produced by powder metallurgy processes involving sintering or deposition from the gas phase by the chemical vapour deposition (CVD) process. The elements have to withstand high loadings - e.g. specific dissipations of 80 W/cm$^2$ or more - and reach very high temperatures of up to approximately 2000$^V$C. Also, they are often used in an atmosphere which, particularly at such high temperatures, is oxidizing or corrosive.

In addition to operating in such conditions, heating elements of this kind are often required to have a predetermined electrical resistance, e.g. of a few tenths of an ohm, at a particular working temperature, they are required to have a predetermined relationship between resistance and temperature over the whole range of temperatures up to the maximum working temperature required, and the elements are also required to have particular geometric domensions, e.g. a particular diameter in the case of an element whose basic shape is that of a circular cylindrical rod. It is often difficult to meet these requirements since the electrical resistance of a heating element and occasionally its temperature/resistance relationship varies during its life as a result of diffusions, more particularly diffusions of the doping atoms or molecules.

It is therefore an object of the invention to provide such a thorough inhibition of such alternations of the electrical resistance and relationship between resistance and temperature during the working life of the element that alterations of these electrical properties do not exceed those that can be tolerated for its particular use.

According to one aspect of the present invention there is provided an electric heating element comprising at least three layers of ceramic material, the first consisting of doped ceramic material and determining the electrical resistance properties of the element, the second being in contact with the first and constituting a barrier layer for inhibiting diffusions into and from the doped layer of particles or atoms or molecules altering the electrical properties of the doped layer and the third layer in being undoped and being in contact with the second layer, the second layer being sandwiched between the first and third layers.

According to a second aspect, the invention provides an electric heating element for use at high loads and having at least three superimposed contacting layers of ceramic material, the electrical resistance of at least one of the layers being reduced by doping below the electrical resistance of an equivalent undoped layer, the heating element having for predetermined geometric domensions a predetermined electrical resistance and, up to a desired working temperature, a predetermined relationship between temperature and the resistance of the element, the doped layer determining the said resistance and the said relationship, one of the layers constituting a barrier layer for inhibiting, at least up to the required working temperature, diffusions into and from the doped layer of particles or atoms or molecules altering the electrical resistance properties of the doped layer, and the remaining one of the layers being undoped and having a thickness which depends on the

required geometric domensions.

According to a third aspect, a method of manufacturing an electric heating element comprises depositing on a substrate a first layer of ceramic material in an environment which causes doping of the layer to reduce the electrical resistance of the layer below that of an equivalent undoped layer, depositing on the first layer a layer of ceramic material having the property of inhibiting diffusions into and from the first layer of particles or atoms or molecules altering the electrical properties of the first layer, and depositing on the second layer a layer of undoped ceramic material.

The electrical properties of the element are determined by the doped layer; preferably, the cross-sectional area of the doped layer depends on the required resistance of the heating element and the concentration of doping agent in the doped layer depends on the required temperature/resistance relationship up to the required working temperature. Increasing the doping agent concentration of the doped layer tends to cause the resistance to increase with increasing temperature and this tendency is superimposed on the known tendency for the resistance of an undoped ceramic layer to decrease with increasing temperature. This makes it possible to select a temperature/resistance characteristic such that the resistance rises or falls or remains constant with rising temperature within the intended working range.

For a given length and for a doping agent concentration which is selected to give the required temperature/resistance characteristic, the resistance of the complete element can be varied within limits by variations of the cross-sectional area of the doped layer. If the cross-sectional area is not constant over the length of the element, e.g. in elements which are in shape trunco-conical but in which the thickness of the doped layer is constant, the resistance of the element is a mean value of the resistance of each of the cross-sectional areas of the elemental parts oand is in such cases determined and designed empirically.

So that a heating element whose geometric dimensions vary over its length may have a very constant resistance over its whole length appropriate technological action which can be determined empirically during the production of the element may be taken to vary the thickness of the doped layer in the various parts of the total length of the element.

The doping agent is selected in the light of technological considerations involved in production of the heating element; an important consideration in selecting any particular doping agent is the availability of an appropriate barrier layer material.

The barrier layer ensures that the doping agent cannot diffuse out of the doped layer in appreciable amounts in the course of time and thus alter at least the resistivities of the doped layer and therefore the resistance of the element. The barrier layer also serves to provide a barrier to the diffusion of atoms or molecules, particularly those of the opposite type of conductivity to that of the doping agents, into the doped layer - e.g. the diffusion into the n-type doped layer of p-conductors which cause recombination of the free charges and therefore changes in the concentration of the electrically effective n-doping. Preferably, - and as far as is technologically possible and/or necessary to observe the required tolerances - the barrier layer consists of a substantially stoichiometrically combined ceramic material which, at least up to the required working temperature, is chemically at least as resistant as the basic material of the doped layer.

If it is to fulfil its function, the barrier layer must be very pure composition and its purity is governed by the technological possibilities and by the required accuracy and constancy of the electrical properties of the element. Purity conditions may be supervised during production by measurement of the electrical resistance by recording current/voltage characteristics, the criterion for purity being that, in the range which is determined by the required tolerances and which determines the requisite outlay on measuring facilities to determine the resistance, the electrical resistance of the element remains virtually unaffected by and during the application of the barrier layer.

Of course, the basic materials of the doped and of the undoped layers may or may not be the same. Similarly, the sequence of the layers in the heating element, which can take the form e.g. of a cylindrical tube, can take the form from inside to outside of a doped layer, a barrier layer and an undoped layer or the converse; the former construction facilitates the observation of predetermined geometric dimensions. If the outermost and/or innermost layer are or is exposed to an atmosphere which is oxidizing and corrosive and alters the electrical properties and which contains e.g. diffusible particles producing or altering n- or p-conductivities, it is advantageous to protect the element, by a further protective or barrier layer, against diffusions, oxidations or corrosions. For instance, an n-doped silicon carbide (SiC(N)) heating element operating in an oxidising atmosphere can be protected by a relatively thin protective or barrier layer of pure silicon oxide.

Preferably, the heating element is produced by the chemical vapour deposition (CVD) process and comprises a hollow member having an inner nitrogen-doped silicon carbide layer (SiC(N)), a titanium nitride (TiN) diffusion barrier layer and an undoped outer silicon carbide layer (SiC).

The invention may be carried into practice in various ways but one heating element and its method of manufacture will now be described by way of example with reference to the accompanying drawings, in which:-

*Figure 1* is a diagrammatic view to an enlarged scale of a hollow cylindrical rod heating element;

*Figure 2* shows the electrical resistance in ohms for a A cm length of heating element plotted against the layer thickness of the growing element - i.e., against the deposition time *t* in minutes; and

*Figure 3* shows the electrical resistance for a 4 cm length of a second heating element in ohms plotted against the temperature in °C.

It will be assumed by way of example that the heating element shown in Figure 1 is required to have a resistance $R_2$ per length portion L of 4 cm of approximately 0.6 ohm at a temperature of approximately 1400°C, the resistance $R_2$ to be substantially independent of temperature in a temperature range of from about 20 to 2000°C. It is also required that the outside diameter D of the hollow rod be approximately 4 mm. It is also required that in use the element be operated in air at temperatures of at least 1600°C, so that the element must be extremely resistant to oxidation.

The required heating element, whose basic material is silicon carbide (SiC), is produced by the CVD process by deposition from the gas phase. To produce the required conductivity, the innermost layer 1 is given an n-conductive doping by means of an addition of nitrogen as doping agent. The reason for choosing nitrogen, which is supplied to the CVD reaction vessel in molecular form, is first because an appropriate material for a barrier layer 2 is available in the form of extremely pure titanium nitride, TiN, and secondly because it is a relatively simple matter to carry the CVD process into effect using gaseous nitrogen as the doping agent. The outermost undoped layer 3 also consists of silicon carbide, SiC.

The element is built up in three consecutive deposition operations; if required the three deposition operations can be performed in three different reaction vessels to ensure that subsequent layers are not accidentally doped or contaminated by residues in the reaction vessel of substances from a previous deposition.

The element is built up from the layers

| 1 | 2 | 3 |
|---|---|---|
| SiC(N) | TiN | SiC |

having layer thicknesses of approximately

0.2 - 0.5, 0.02 - 03, and 0.5 - 0.8 mm

by deposition on an electrically heated graphite rod or 2 mm diameter at atmospheric pressure and at a rod temperature of 1400°C, the latter temperature being measured by a pyrometer and being maintained constant by varying the heating current flowing through the graphite.

The gas phases from which the discrete ingredients of the layers deposit consecutively are gas mixtures of the following composition:

For the layer 1:

trichloromethylsilane $CH_3SiCl_3$/hydrogen $H_2$/nitrogen $N_2$

For the barrier layer 2:

titaniumtetrachloride $TiCl_4$/hydrogen $H_2$/nitrogen $N_2$

For the outer layer 3:

trichloromethylsilane $CH_3SiCl_3$/hydrogen $H_2$/argon Ar.

The flow of nitrogen is required both as carrier for the $CH_3SiCl_3$ or $TiCl_4$ vapours and to dope the conductive layer 1 and to form the barrier layer 2 from TiN. The flow of hydrogen serves as a reducing agent for the intermediate products which have to be reduced, and the argon serves as a carrier and provides an inert gas atmosphere in the reactor vessle.

To ensure uniform deposition in all directions, the gases and vapours are delivered through three tubes disposed uniformly around and parallel to the graphite member, the tubes being formed at regular intervals throughout their length with nozzle orifices in their walls facing the graphite rod.

The production conditions, e.g. the rates of flow of the vapours and gases, are of course optimized experimentally by means of appropriate repliminary experiments, to ensure great uniformity in the deposited diameter and in electrical resistance over the whole length of the element.

For the present case the process conditions tabulated hereinafter have been found to be optimal, although the values given depend upon the particular apparatus used and are therefore not universally valid.

| Rate of flow in litres/min: | SiC(N) | TiN | SiC |
|---|---|---|---|
| $N_2$ over $CH_3SiCl_3$ (40°) | 0.4 | | |
| $N_2$ over $TiCl_4$ (20°) | | 1.4 | |
| Ar over $CH_3SiCl_3$ (50°) | | | 0.1 |
| $H_2$ | 2.0 | 0.8 | 3.4 |
| Temperature (°C) | | | |
| 1400 | | | |
| 1400 | | | |
| 1400 | | | |
| Pressure (atm) | 1 | 1 | 1 |
| Deposition time (minutes) | 25 | 15 | 35 |
| Layer thickness (mm) | 0.44 | 0.025 | 0.54 |

The temperature stated for the rate of flow of nitrogen and argon relate to the temperature which exists in the supply vessel for trichloromethylsilane or titanium-tetrachloride and which determines the vapour pressure - and therefore, in association with the flow of carrier gas, the rates of flow - of these substances.

The deposition time for the first layer is determined by the required electrical resistance, and the deposition time for the third layer is determined by the required geometric diameter of the finished element. In an advantageous procedure for producing the doped layer, the nitrogen concentration necessary for the required temperature dependence of the electrical resistance of the element - i.e., the rate of nitrogen flow - is first determined empirically from experience, whereafter the cross-sectional area necessary for the required resistance or, for a given geometric value of the graphite substrate, the required thickness of the doped layer I, is calculated from the electrical resistance measured for a particular cross-sectional area at this nitrogen concentration, whereafter the necessary deposition time is determined in the light of the predetermined rates of gas and vapour flow.

As already stated, the purity of the titanium nitride diffusion barrier layer 2 is also determined experimentally; the purity criterion i.e. the criterion that the correct relationship between the rates of nitrogen and titanium tetrachloride flow for deposition of the barrier layer has been reached - is that during deposition of the barrier layer there is little, if any, change in the measured electrical resistance. The rate of titanium tetrachloride flow can be controlled through the agency of the rate of carrier gas flow and through the agency of the temperature in the supply tank, the latter temperature determining the vapour pressure of the titanium tetrachloride; conveniently too, the titanium tetrachloride is reduced completely by means of the hydrogen, so that if only a single reaction vessel is used to prepare all the layers, there is no possible risk of subsequent contamination of the third layer by incompletely reduced residues of titanium chloride left in the vessel. Accordingly, an adequately large rate of hydrogen flow must be available to ensure complete reduction of the titanium chloride.

Similarly, the composition of the undoped outer layer, whose purity also depends upon the technological and economic aspects mentioned, is supervised by ensuring that the electrical resistance of the heating element does not vary during production.

As will be apparent from the foregoing, the electrical resistance of the growing element must be supervised during the deposition of each of the three layers. Supervision is by means of a current/voltage measurement followed by calculation based on Ohm's Law; the resistance thus determined is the result of connecting the known resistance $R_1$ of the graphite substrate in parallel with the required resistance $R_2$ of the heating element being formed by deposition. The relationship-

$$1/R = 1/R_1 + 1/R_2$$

therefore applies.

Referring to the diagram in Figure 2, curve *a*, in which the solid circles indicate measuring points, represents the total electrical resistance R as hereinbefore described and plotted against the deposition time *t* in minutes during the production of a heating element in the manner described and using the process data quoted. The scale on the left-hand ordinate axis is associated with the curve *a*. Indicated at the top of the diagram are the periods of time occupied by the production of the three different layers. The empty circles, the bottom curve *b* and the associated scale on the right-hand side of Figure 2 indicate the resistance $R_2$ of the heating element when it has been separated from the graphite core, the heating element having a length L of 4 cm.

Figure 3 shows the temperature in °C plotted against the resistance $R_2$ of a second heating element having a length L of 4 cm in ohms. As will be apparent, up to a temperature of 2000°C the resistance has only very small temperature-dependent variations.

Further investigation has shown that the chemical and the electrical stability of the heating element - i.e. when the same is used in air, more particularly its resistance to oxidation and in particular its resistance to diffusion of doping agent out of the doped layer - is very high up to temperatures of approximately 2000°C; consequently, the element has a longer working life than elements made of sintered silicon carbide, yet there is little significant charge in the electrical properties of the element during its working life. Preferably the material of the barrier layer is chemically at least as resistant as the basic material of the doped layer. A second barrier layer may be provided, in similar fashion, on the side of the doped layer remote from the first barrier layer.

WHAT WE CLAIM IS:-

1. An electric heating element comprising at least three layers of ceramic material, the first consisting of doped ceramic material and determining the electrical resistance properties of the element, the second being in contact with the first and constituting a barrier layer for inhibiting diffusions into and from the doped layer of particles or atoms or molecules altering the electrical properties of the doped layer and the third layer being undoped and being in contact with the second layer undoped, the second layer being sandwiched between the first and third layers.

2. An electric heating element for use at high loads and having at least three suprimposed contacting layers of ceramic material, the electrical resistance of at least one of the layers being reduced by doping below the electrical resistance of an equivalent undoped layer, the heating element having for predetermined geometric dimensions a predetermined electrical resistance and, up to a desired working temperature, a predetermined relationship between temperature and the resistance of the element, the doped layer determining the said resistance and the said relationship, one of the layers constituting a barrier layer for inhibiting, at least up to the required working temperature, diffusions into and from the doped layer of particles or atoms or molecules altering the electrical resistance properties of the doped layer, and the remaining one of the layers being undoped and having a thickness which depends on the required geometric dimensions.

3. A heating element as claimed in Claim 2 in which the cross-sectional area of the doped layer depends on the required resistance of the heating element and the concentration of doping agent in the doped layer depends on the required relationship between temperature and the resistance of the element up to the required working temperature.

4. A heating element as claimed in any one of the preceding Claims in which the barrier layer is made of a pure ceramic material which, at least up to the required working temperature, is chemically at least as resistant as the basic material of the doped layer.

5. A heating element as claimed in any of the preceding Claims in which different ceramic materials are used for the basic material of the doped layer and of the undoped layer.

6. A heating element as claimed in any one of the preceding Claims in which the layers are annular and one within aother, the layers, proceeding from inside to outside, being in the order a doped layer, a barrier layer and an undoped layer.

7. A heating element as claimed in any of the preceding Claims in which there is a second barrier layer on the side of the doped layer remote from the first barrier layer.

8. A heating element as claimed in any of the preceding Claims which is produced by a chemical vapour deposition process and constitutes a hollowmember having an inner nitrogen-doped silicon carbide layer, a titanium nitride diffusion barrier layer and an undoped outer silicon carbide layer.

9. A heating element substantially as described herein with reference to the accompanying drawings.

10. A method of manufacturing an electric heating element which comprises depositing on a substrate a first layer of ceramic material in an environment which causes doping of the layer to reduce the electrical resistance of the layer below that of an equivalent undoped layer, depositing on the first layer a layer of ceramic material having the property of inhibiting diffusions into and from the first layer of particles or atoms or molcules altering the electrical properties of the first layer, and depositing on the second layer a layer of undoped ceramic material.

KILBURN & STRODE,
Chartered Patent Agents,
Agents for the Applicants.

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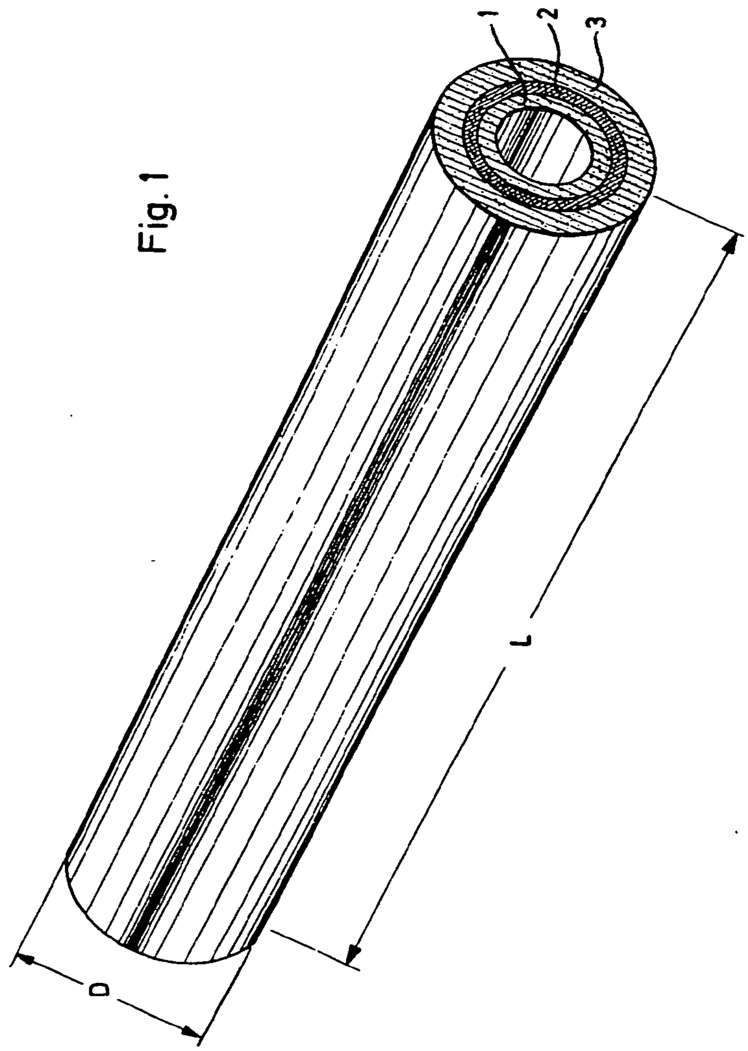
Fig. 1



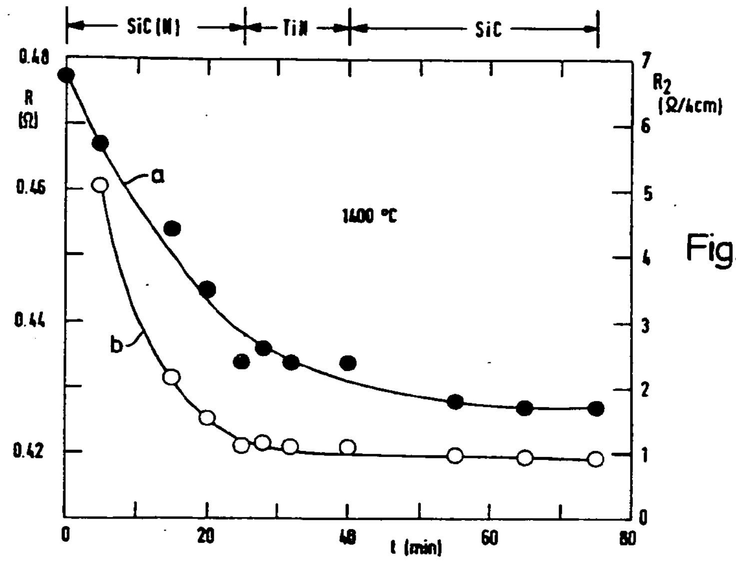

SiC (N)
TiN
SiC
0.48
R
(Ω)
0.46
0.44
0.42
7
$R_2$
(Ω/4cm)
6
5
4
3
2
1
0
a
b
1400 °C
0
20
40
60
80
t (min)

Fig. 2

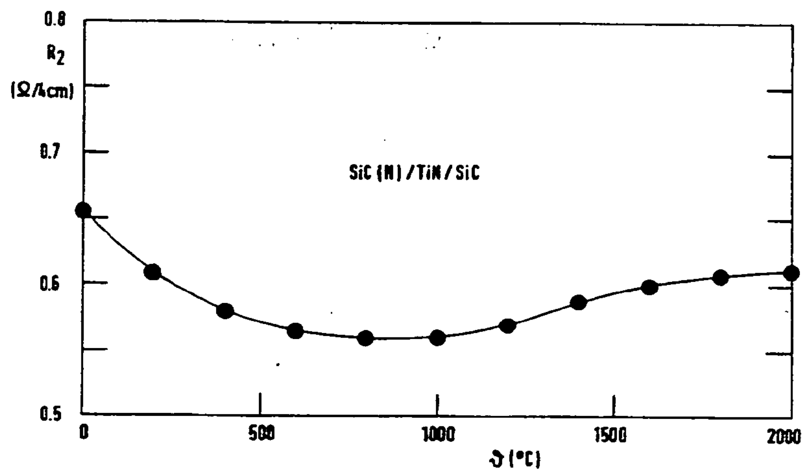

0.8
$R_2$
(Ω/4cm)
0.7
0.6
0.5
SiC (N) / TiN / SiC
0
500
1000
1500
2000
ϑ (°C)

Fig. 3